

Effect of Wax Content in Hydrocracker Unconverted Oil on Viscosity Index and Yield of Lubricant Base Oil 150N

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ABSTRACT

Hydroprocessing has become the main technology for the production of API Group II and III base oils. One of the key properties is viscosity index for Group II and III base oils. The effect of wax content in hydrocracker unconverted oil on viscosity index and yield was studied in a 400 kton/year hydroisomerization dewaxing plant at a total pressure of 15 MPa, a feed rate of 38 ton/hour, and a gas to oil ratio of $710 \text{ Nm}^3(\text{H}_2)/\text{m}^3(\text{feed})$. The contribution of wax hydroisomerization to the viscosity index of the main product 150N base oil increases with the wax content in the 11-19% range and reaches a constant value of 6 VI units rather than continuously rising with the wax content. The 150N yield decreases about 1.3%, when the wax content increases by 1%. This is related to a higher dewaxing temperature required at increased wax contents in order to keep the low pour point of 150N, which results in more multi-branched compounds with a low viscosity index in the base oils and more light hydrocracking products.

Keywords: Mineral Base Stock Refining, Hydroisomerization Dewaxing, Base Oil, Viscosity Index

INTRODUCTION

Based on the viscosity index, sulfur, and saturates content, mineral base oils are divided into Group I, II, and III by API. With the emphasis on energy conservation and environment protection, Group I base oils have been gradually replaced by Group II and III base oils because of good oxidative stability, high viscosity index, low sulfur, low nitrogen, and low aromatic content. Group II and Group III base oils are used in many lubricant products such as high grade engine oil, hydraulic oil, turbine oil, and so on [1-5]. The process of producing Group II and III base oils is gradually switching from solvent refining, solvent dewaxing, and clay refining to hydrogenation technology [6-9]. At present, all the

hydroprocessing technologies used to produce Group II and III base oils mainly include hydrocracking, hydroisomerization dewaxing, and hydrofinishing processes coupled with atmospheric and vacuum distillation. The heavy fraction of petroleum is first hydroprocessed in a hydrocracking unit to get hydrocracker unconverted oil (UCO) with low sulfur, low nitrogen, and low metal content. Then, the pour point of UCO is reduced by hydroisomerizing normal paraffins present in the feed to isoparaffins; finally, it goes through a hydrofinishing process for aromatics saturation to improve oxidative stability. The whole liquid product from hydroprocessing is finally separated

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by atmospheric and vacuum distillation to get base oil products [10-11]. The effects of hydrocracking option (one stage versus two stages), hydrogen pressure, and hydrotreating temperature on the content of sulfur, nitrogen, and aromatics in the base oils have been reported [12]. The relationship between the feed rate of UCO and hydroisomerization dewaxing reaction temperature was also studied [13]. However, up to now, published literature about the effect of wax content in the UCO on the viscosity index and the yield of base oil is very limited.

For base oil hydroprocessing, a plant with a capacity of 400 (kton/year) in the CNOOC Petrochemicals Branch Company started operating in May 2011, and the principle process scheme is shown in Figure 1.

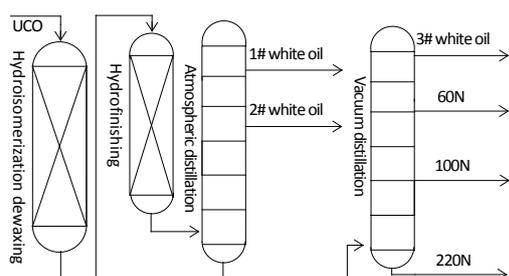


Figure 1: Principle process diagram of base oil hydroprocessing unit.

The two base oil products, 100N and 220N, are blended completely on line to produce the main product 150N to meet market needs. The fluctuation of wax content in the UCO feed has an important impact on viscosity index and yield of 150N. To study the impact of wax content, UCO feeds with different wax contents were chosen as experimental feeds. The dewaxing plant was kept in stable operating conditions except for the dewaxing reactor temperature. The main product 150N has almost the same properties except for the viscosity index. The results obtained for the effect of wax content in the UCO on viscosity index and the yield of 150N are used for CNOOC to choose suitable UCO for

the dewaxing unit.

EXPERIMENTAL PROCEDURES

Hydroisomerization dewaxing section involves hydrocracking and other side reactions in addition to hydroisomerization dewaxing as the main reaction. In order to only study the effect of wax content in the UCO on the viscosity index and the yield of 150N, six batches of UCO, in which sulfur and nitrogen content, are both below 1 mg/kg and UV absorption and polycyclic aromatic index are similar, and chosen as the experiment feed. The distillation data indicates that the UCO feeds have similar heavy fraction, which was the source of the main base oil product. In order to get the wax content in the UCO, the sample of six batches of UCO experiment feed are dewaxed with a solvent dewaxing process in laboratory until the pour point of the rest of UCO (dewaxed oil) is $-17\text{ }^{\circ}\text{C}$, which tends to be consistent with the pour point of 150N. Meanwhile, the viscosity index of the dewaxed oil is obtained and all the data are presented in Table 1, which shows that the viscosity index and pour point of the UCO increase with the wax content in the UCO. The experiments were carried out in the $400\frac{\text{kt}}{\text{year}}$

base oil hydroprocessing unit. The temperature, pressure, feed rate, and H_2 to oil ratio of hydroisomerization dewaxing section have important influences on wax isomerization reaction. According to unit design and the market requirement of 150N, the parameters except for temperature are almost fixed and listed in Table 2. With an increase in the wax content in the UCO, increasing the feed inlet temperature of the hydroisomerization dewaxing section is an effective way to raise hydroisomerization dewaxing reaction rate for ensuring the low pour point of 150N. At the same time, the reaction heat will lead to a rise in temperature in the axial direction of reactor beds.

Table 1: Properties of six batches of UCO experiment raw material.

Item	UCO-1	UCO-2	UCO-3	UCO-4	UCO-5	UCO-6
Kinematic viscosity at 100 °C (mm ² /s)	4.00	3.98	4.09	4.04	3.97	3.96
Kinematic viscosity at 40 °C (mm ² /s)	18.79	18.03	18.26	17.86	17.09	16.72
Nitrogen content (mg/kg)	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Sulfur content (mg/kg)	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Distillation temperature (°C)						
0.5%	192.3	194.5	193.5	190.4	194.4	195.6
50%	412.6	412.1	411.8	412.6	412.8	413.0
90%	480.5	483.2	479.1	477.0	476.8	476.3
99.5%	562.9	561.6	561.2	564.6	562.3	563.6
UV Absorption						
226 nm	2.922	2.504	2.106	2.238	2.495	2.276
385 nm	0.03290	0.03395	0.03672	0.03422	0.04038	0.03674
435 nm	0.00384	0.00467	0.00328	0.00359	0.00971	0.00589
Polycyclic aromatic index	274	280	309	286	319	300
Pour point (°C)	31	32	33	34	34	35
Viscosity index	110	118	126	127	132	137
Wax content in the UCO (wt %)	11.29	13.45	14.80	15.61	16.69	18.61
Pour point of dewaxed oil (°C)	-17	-17	-17	-17	-17	-17
Viscosity index of dewaxed oil	104	104	108	108	109	113

The hydroisomerization dewaxing reactor is composed of three beds. The temperatures at the top level and the bottom level of the first, the second, and the third bed, which are the arithmetic mean of four temperature values measured by thermocouples at the same elevation, are respectively expressed with T_{10} , T_{11} , T_{20} , T_{21} , T_{30} , and T_{31} . The reaction temperature T is calculated according to Equation 1.

$$T = \frac{T_{10} + T_{11}}{2} \times a + \frac{T_{20} + T_{21}}{2} \times b + \frac{T_{30} + T_{31}}{2} \times c \quad (1)$$

where, a , b , and c represents respectively the volume fraction of the active catalyst in the first, second, and third beds. The inlet temperature and calculated reaction temperature in the experiments are also tabulated in Table 2.

The main operation parameters in hydrofinishing, atmospheric distillation, and vacuum distillation sections are also kept to be basically similar.

RESULTS AND DISCUSSION

The properties and yield of 150N corresponding to the experiment feeds are listed in Table 3. The viscosity at 100 °C and pour points are from 5.25 mm²/s to 5.35 mm²/s and from -16 °C to -17 °C respectively. The open cup flash point is higher than 220 °C and the distillation range is similar. The saturated hydrocarbon content is more than 99.5% and the sulfur content is less than 1 mg/kg. This means that the properties of 150N are nearly similar except for the viscosity index. The viscosity index of 150N is determined by two factors, namely the viscosity index of the dewaxed oil in the UCO and the viscosity index of isoalkanes, which are the products of wax hydroisomerization.

The difference in viscosity index between 150N and the dewaxed oil can be considered as the

contribution value of wax hydroisomerization to the viscosity index of 150N. As shown in Table 4, the contribution of the wax content to viscosity index increases from 3 units at lower wax contents to 6 units at higher wax contents, but it reaches a plateau at about 5 units with a further increase in the wax content in the UCO. The trend of the contribution of wax to 150N viscosity index can also be seen in Figure 2.

Data from Table 1 and Table 3 are also shown in Figure 3. The relationship between the wax content in the UCO and the yield of 150N can be roughly expressed by a linear regression equation of $Y = -1.27X + 85.1$, that is, the yield of 150N drops by about 1.3%, when the wax content increases by 1%. In contrast to the decrease in 150N yield, the yield of lighter lubricants (2-3 cSt oil) rises accordingly.

Table 2: Main operating parameters of hydroisomerization dewaxing section.

Item	UCO-1	UCO-2	UCO-3	UCO-4	UCO-5	UCO-6
Feed rate (ton/hour)	37.92	38.05	38.05	38.90	38.03	38.35
H ₂ to oil ratio (Nm ³ /m ³)	739.12	737.77	725.90	722.55	713.51	720.72
Total pressure (MPa)	15.00	15.00	15.00	15.00	15.00	15.00
Inlet temperature (°C)	312.76	313.82	317.43	319.85	322.53	324.92
Reaction temperature (°C)	328.74	330.06	333.89	335.75	336.79	338.84

Table 3: Properties and yield of 150N.

Item	UCO-1	UCO-2	UCO-3	UCO-4	UCO-5	UCO-6
Pour point (°C)	-17	-16	-17	-17	-16	-17
Kinematic viscosity at 40 °C (mm ² /s)	30.51	29.78	29.82	29.37	29.24	29.06
Kinematic viscosity at 100 °C (mm ² /s)	5.32	5.26	5.34	5.29	5.31	5.34
Viscosity index	107	108	113	113	115	118
Open cup flash point (°C)	221	225	224	220	224	222
Vap. %	Distillation temperature (°C)					
0.5%	347.6	346.2	346.4	354.2	356.2	355.8
50%	426.7	424.8	426.6	427.6	427.9	427.9
90%	497.0	508.0	510.6	497.9	496.7	492.6
99.5%	569.8	570.0	570.4	569.0	568.4	566.1
Saturated hydrocarbon content (wt %)	>99.5	>99.5	>99.5	>99.5	>99.5	>99.5
Yield (wt %)	69.99	69.18	67.66	64.17	62.35	62.12

Table 4: Contribution of wax hydroisomerization to the viscosity index of 150N.

Item	UCO-1	UCO-2	UCO-3	UCO-4	UCO-5	UCO-6
Wax content in the UCO (wt %)	11.29	13.45	14.80	15.61	16.69	18.61
Viscosity index of dewaxed oil	104	104	108	108	109	113
Viscosity index of 150N	107	108	113	113	115	118
Difference of viscosity index	3	4	5	5	6	5

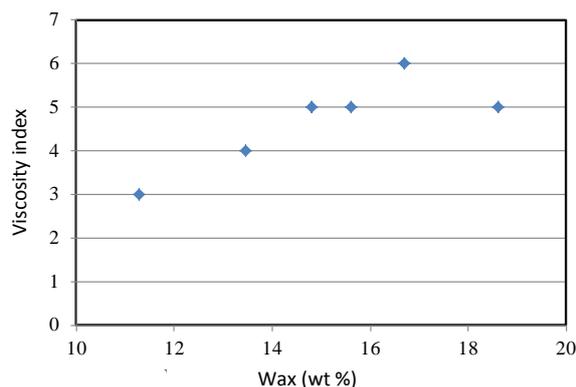


Figure 2: A rise in viscosity index of 150N with UCO wax content.

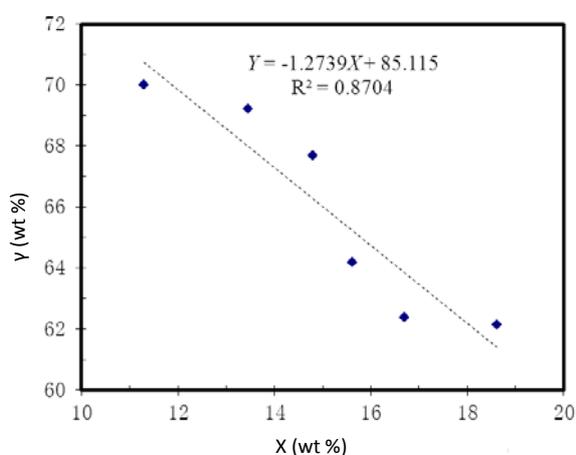


Figure 3: Yield of 150N with wax content in the UCO.

The low temperature performance of *n*-paraffins is poor and its melting point increases by molecular weight, but it has a high viscosity index. The removal of *n*-paraffins in the feed with a solvent dewaxing process may reduce the pour point, but the viscosity index and the yield of base oil are reduced simultaneously. The hydroisomerization dewaxing process converts *n*-paraffins to isoparaffins to improve base oil low temperature flow properties. For example, the melting temperature of hexadecane is 19 °C, while its isomer 5-methylpentadecane melts at -31 °C. Another example is 1-docosylcyclohexane melting at 49 °C, while 2-decyldodecylcyclohexane melts at -4 °C [14]. With increased wax content in the UCO, in order to improve the conversion of *n*-paraffins, it is necessary to raise the hydroisomerization dewaxing reaction temperature or to decrease the

feed rate. However, increasing reaction temperature is usually adopted to ensure the output of the hydroprocessing unit. From Table 1 and Table 2, the relationship between the wax content in the UCO and hydroisomerization dewaxing reaction temperature can be expressed, as shown in Figure 4, by a linear regression equation of $T = 1.5X + 311.3$, that is, the hydroisomerization dewaxing reaction temperature should be increased by 1.5 °C, when the wax content rises by 1% to keep the 150N pour point in the range of -16 °C to -17 °C.

The main function of the hydroisomerization dewaxing catalyst in the hydroprocessing unit is the isomerization of *n*-paraffins, but it also contributes to the hydrocracking of *n*-paraffins. Figure 5 is the schematic diagram of hydroisomerization/hydrocracking of C_{21} *n*-paraffin.

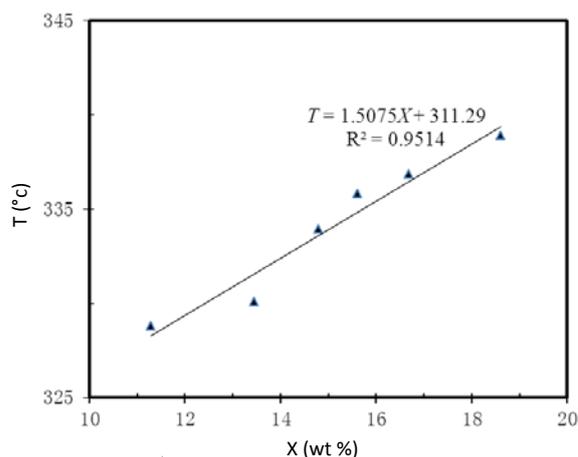


Figure 4: Reaction temperature versus wax content in the UCO.

According to the bifunctional mechanism, the hydroisomerization and hydrocracking of *n*-paraffins occur through a series of consecutive reactions, where the cracking products are mainly formed through β -scission of di- and multibranched isoalkanes [15], while these isoalkanes, except for the partly multibranched isoalkanes with a low viscosity index, are a class of compounds which need to be preserved to produce base oil with a high viscosity index and a low pour point.

The rise in hydroisomerization dewaxing reaction temperature not only can improve the conversion

of *n*-paraffins, but also can increase the reaction rate of hydrocracking. More isoalkanes are hydrocracked into short-chain hydrocarbons and the yield of 150N decreases with increasing wax content in the UCO. The result is consistent with that of increasing conversion of *n*-paraffins, which results in a decrease in the average carbon number of molecular chain and thus the base oils become lighter [16]. At the same time,

the increased conversion of *n*-paraffins causes the average branching number in molecular structure to grow [16], and thus more multibranched isoalkanes with a low viscosity index are formed. Therefore, once increasing the wax content in the UCO, the contribution of wax hydroisomerization to the viscosity index of 150N reaches a value of 6 units rather than continuously increasing.

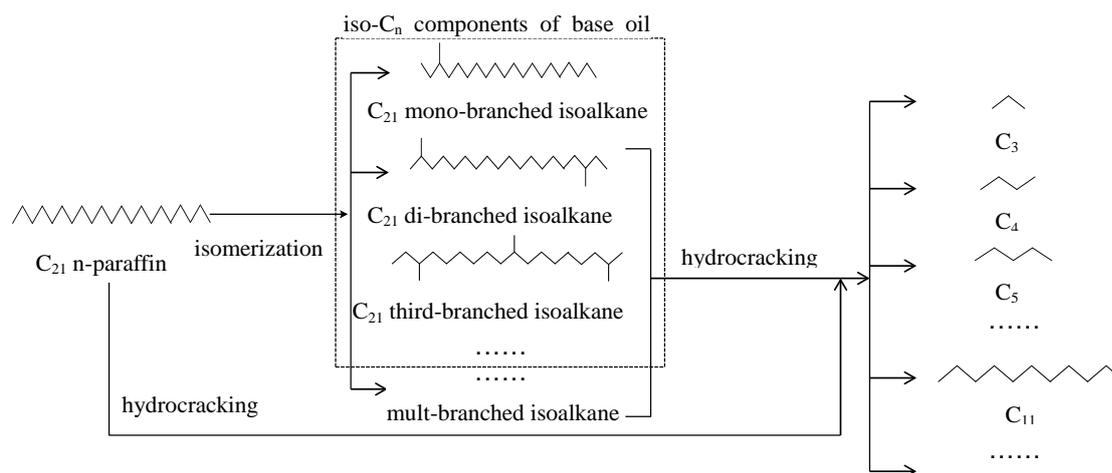


Figure 5: A schematic diagram of hydroisomerization / hydrocracking of C_{21} *n*-paraffin.

CONCLUSIONS

All hydroprocessing technologies have been gradually used for producing Group II and III base oils. The composition and properties of UCO feed have important effects on the properties and yield of base oil. According to the experimental results in the present paper, the hydroisomerization dewaxing reaction temperature should be increased 1.5 °C in order to meet the low pour point requirement of the main product 150N, when the wax content in the UCO increases by 1%. Raising the reaction temperature simultaneously leads to more multibranched compounds with a low viscosity index and causes the reaction rate of hydrocracking to increase; the contribution of wax hydroisomerization to the viscosity index of 150N reaches the maximum value of 6 units by raising the wax content in the UCO, while the yield of 150N drops by about 1.3% by an increase of 1% in the wax content in the UCO, which is also accompanied by a higher yield

of light base oils.

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REFERENCES

- [1] Adhvaryu A., Erhan S. Z., and Sahoo S. K., "Thermo-oxidative Stability Studies on Some New Generation API Group II and III Base Oils," *Fuel*, **2002**, 81(6), 785-791.
- [2] Sharma B. K., Adhvaryu A., and Sahoo S. K., "Influence of Chemical Structures on Low-Temperature Rheology, Oxidative Stability, and Physical Properties of Group II and III Base Oils," *Energy and Fuels*, **2004**, 18(4), 952-959.
- [3] Ryan H. T., "Use of Group II, Group III Base Stocks in Hydraulic and Industrial Applications," *Industrial Lubrication and*

- Tribology*, **1999**, 51(6), 287-293.
- [4] Gatto V. J., Moehle W. E., and Cobb T. W., "The Relationship between Oxidation Stability and Antioxidant Depletion in Turbine Oils Formulated with Groups I, II, III and IV Base Stocks," *J. Synthetic Lubrication*, **2007**, 24(2), 111-124.
- [5] Glenn T. F. and Cosgriff W. L., "The Outlook for Group II/II and Group III Base Oils in the U.S. Grease Market," *NLGI Spokesman*, **2002**, 66(6), 14-19.
- [6] Sarpal A. S., Sastry M. I. S., and Bansal V., "Correlation of Structure and Properties of Group I to III Base Oils," *Lubrication Science*, **2012**, 24(5), 199-215.
- [7] Sharma B. k., Adhvaryu A., and Perez J. M., "Effects of Hydroprocessing on Structure and Properties of Base Oils using NMR," *Fuel Processing Technology*, **2008**, 89(10), 984-991.
- [8] Anwar M., Kaushik R. S., and Srivastava M., "Basics: Current Base Oil Quality and Technological Options for its Improvement-an Overview," *Lubrication Science*, **2002**, 14(4), 425-434.
- [9] Levina L. A., Zelentsov Yu. N., and Elshin A. I., "Catalyst System for Hydrorefining of Base Oils," *Khimiya i Tekhnologiya Topliv i Masel*, **2003**, 4, 14-15.
- [10] Lei G. D., Dahlberg A., and Krishna K., "All Hydroprocessing Route to High Quality Lubricant Base Oil Manufacture Using Chevron Isodewaxing Technology," *AIChE Annual Meeting, Conference Proceedings*, **2008**.
- [11] Kim G. R., Kim C. K., and Kim, I. C., "Method for Producing Feedstocks of High Quality Lube Base Oil from Unconverted Oil," U.S. Patent 20090050524, **2009**.
- [12] Galiano-Roth A. S. and Page N. M., "Effect of Hydroprocessing on Base Stock Composition and Product Performance," *Lubri. Eng.*, **1994**, 50(8), 659-664.
- [13] Lin R. X. and Liu Y., "Industrial Application of Hydrocracked Tail Oil as Feedstock for Lubricating Oil Hydrogenation," *Petroleum Processing and Petrochemicals*, **2012**, 43(3), 6-10
- [14] Calemma V., Peratello S., and Stroppa F., "Hydrocracking and Hydroisomerization of Long-Chain *n*-Paraffins Reactivity and Reaction Pathway for Base oil Formation," *Ind. Eng. Chem. Res.*, **2004**, 43, 934-940.
- [15] Pellegrini L. A., Gamba Simone., and Bonomi Susi., "Equilibrium Constants for isomerization of *n*-Paraffins," *Ind. Eng. Chem. Res.*, **2007**, 46, 5446-5452.
- [16] Kobayashi M., Saitoh M., and Ishida K., "Viscosity Properties and Molecular Structure of Lube Base Oil Prepared from Fischer-Tropsch Waxes," *J. Jpn. Petrol. Inst.*, **2005**, 48(6), 365-372.